ORGANIC CHEMISTRY

JOHN McMURRY *Cornell University*

Brooks/Cole Publishing Company *Monterey, California*

Brooks/Cole Publishing Company
A Division of Wadsworth, Inc.

Printed in the United States of America

10 9 8 7 6

Library of Congress Cataloging in Publication Data

McMurry, John.
Organic chemistry.

(The Brooks/Cole series in chemistry)
Includes index.
1. Chemistry, Organic. I. Title. II. Series.
QD251.2.M43 1984 547 83-7744

ISBN 0-534-01204-3

Sponsoring Editor: Michael Needham
Editorial Assistant: Lorraine McCloud
Production Service: Phyllis Niklas
Production Coordinator: Joan Marsh
Manuscript Editor: Gloria Joyce
Interior and Cover Design: Stan Rice
Interior Illustration: Vantage Art, Inc.
Typesetting: Jonathan Peck Typographers, Ltd.

On the Cover: The cover drawings of a molecule recently synthesized at Cornell University were provided by Molecular Design Limited, Hayward, California. They were generated by the MACCS® and SPACFIL computer programs for the storage, retrieval, modeling, and display of chemical structures. (Additional airbrush background by Tim Keenan.)

PREFACE

The 1970s and early 1980s were a time of rapid change for the science of organic chemistry; physical organic chemists provided us with a deeper understanding of organic reactivity, and synthetic organic chemists provided us with many selective new reactions and reagents. Organic chemistry texts also underwent changes in this period, but of a largely pedagogical sort. Thus, good teaching texts today make effective use of two-color printing and three-dimensional airbrushed art; they use many stereochemical drawings; and they provide teaching aids such as chapter summaries, reaction summaries, and extensive problem sets of graded difficulty.

My goal in writing this book has been to combine coverage of the many exciting scientific advances of the last decade with the equally important pedagogical advances that have been made. I have attempted to write a lucid, readable, and effective *teaching* text while providing an accurate and up-to-date view of organic chemistry as it is understood and practiced in the mid-1980s.

Organization

This book uses a dual functional-group/reaction-mechanism organization. The primary organization is by functional group, beginning in Chapter 5 with the simple (alkenes) and going on to the more complex. Within this primary organization, however, heavy emphasis is placed on explaining the mechanistic similarities of reactions. Indeed, many chapters, such as Chapter 22, "Aldehydes and Ketones: Nucleophilic Addition Reactions," and Chapter 24, "Carboxylic Acid Derivatives and Nucleophilic Acyl Substitution Reactions," even have dual functional-group/reaction-mechanism titles.

Organic molecules and organic reactions are presented as early as possible. After a brief review of structure, bonding, and molecular properties in Chapters 1 and 2, organic molecules and functional groups are introduced in Chapter 3. An introduction to the nature of organic reactions then follows in Chapter 4.

Insofar as possible, the topics have been arranged in a modular way. Thus, the chapters on spectroscopy are grouped together (Chapters 11–13), the chapters on aromatic chemistry are grouped together (Chapters 14–16), and the chapters on carbonyl compounds are grouped together (Chapters 21–26). This organization not only brings cohesiveness to these subjects, it allows the instructor the flexibility to teach them in an order different from

TABLE 21.1 **Some common types of carbonyl compounds**

Name	*General formula*	*Name ending*
Aldehyde	$R-\overset{\overset{O}{\|}}{C}-H$	*-al*
Ketone	$R-\overset{\overset{O}{\|}}{C}-R'$	*-one*
Carboxylic acid	$R-\overset{\overset{O}{\|}}{C}-O-H$	*-oic acid*
Acid chloride	$R-\overset{\overset{O}{\|}}{C}-Cl$	*-yl* or *-oyl chloride*
Acid anhydride	$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$	*-oic anhydride*
Ester	$R-\overset{\overset{O}{\|}}{C}-O-R'$	*-oate*
Lactone (cyclic ester)	$\underbrace{>C-\overset{\overset{O}{\|}}{C}-O}$	None
Amide	$R-\overset{\overset{O}{\|}}{C}-N<$	*-amide*
Lactam (cyclic amide)	$\underbrace{>C-\overset{\overset{O}{\|}}{C}-N}<$	None

It is very useful to classify carbonyl compounds into two general categories, based on the kinds of chemistry they undergo:

Aldehydes Ketones	The acyl units in these two functional groups are bonded to substituents (H and R, respectively) that *cannot serve as leaving groups*. Aldehydes and ketones therefore behave similarly and undergo many of the same reactions.
Carboxylic acids Esters Acid chlorides Acid Anhydrides Amides	The acyl units in carboxylic acids and their derivatives are bonded to substituents (oxygen, halogen, nitrogen) that *can serve as leaving groups* in substitution reactions. The chemistry of these compounds is therefore similar.

21.2 Nature of the carbonyl group

The carbon–oxygen double bond of carbonyl groups is similar in many respects to the carbon–carbon double bond of alkenes (Figure 21.1). The

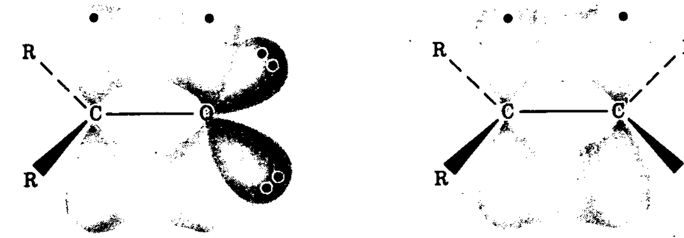
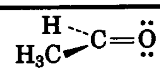


Figure 21.1. Electronic structure of the carbonyl group.

carbonyl carbon atom is sp^2 hybridized and forms three sigma bonds. The fourth valence electron remains in a carbon *p* orbital and forms a pi bond to oxygen by overlap with an oxygen *p* orbital. The oxygen atom also has two nonbonding pairs of electrons, which occupy its remaining two orbitals. (The oxygen atom is probably sp^2 hybridized, though there is some disagreement about this point.)

Like alkenes, carbonyl compounds are planar about the double bond and have bond angles of approximately 120°. Table 21.2 shows the structure of acetaldehyde and indicates the experimentally determined bond lengths and angles. As we would expect, the carbon–oxygen double bond is shorter (1.22 Å versus 1.43 Å) than the normal carbon–oxygen single bond; it is also stronger (175 kcal/mol versus 92 kcal/mol).

TABLE 21.2 Structure of acetaldehyde



Bond angle (degrees)		*Bond length (Å)*	
H—C—C	118	C=O	1.22
C—C—O	121	C—C	1.50
H—C—O	121	OC—H	1.09

Carbon–oxygen double bonds are polarized $C^{\delta+}—O^{\delta-}$ because of the high electronegativity of oxygen relative to carbon, and carbonyl compounds therefore have substantial dipole moments. Table 21.3 lists the observed dipole moments for a variety of different types of carbonyl compounds and indicates that all are strongly polarized.

The most important consequence of carbonyl-group polarization is the chemical reactivity of the carbon–oxygen double bond. Since the carbonyl carbon is positively polarized, it is an electrophilic site and is attacked by nucleophiles. Conversely, the carbonyl oxygen is negatively polarized and is a nucleophilic (basic) site.